



# Photocatalytic recovery of H<sub>2</sub> from H<sub>2</sub>S containing wastewater: Surface and interface control of photo-excitons in Cu<sub>2</sub>S@TiO<sub>2</sub> core-shell nanostructures

V. Navakoteswara Rao<sup>a</sup>, N. Lakshmana Reddy<sup>a</sup>, M. Mamatha Kumari<sup>a</sup>, P. Ravi<sup>b</sup>, M. Sathish<sup>b</sup>, K.M. Kuruvilla<sup>c</sup>, V. Preethi<sup>c,\*</sup>, Kakarla Raghava Reddy<sup>d</sup>, Nagaraj P. Shetti<sup>e,f</sup>, Tejraj M. Aminabhavi<sup>f,g,\*</sup>, M.V. Shankar<sup>a,\*\*</sup>

<sup>a</sup> Nanocatalysis and Solar Fuels Research Laboratory, Department of Materials Science & Nanotechnology, Yogi Vemana University, Kadapa, Andhra Pradesh, 516005 India

<sup>b</sup> Functional Materials Division, Central Electrochemical Research Institute (CSIR-CECRI), Karaikudi, Tamil Nadu, 630003 India

<sup>c</sup> Department of Civil Engineering, Hindustan Institute of Technology and Science, Padur, Chennai, Tamil Nadu, 603103 India

<sup>d</sup> School of Chemical and Biomolecular Engineering, The University of Sydney, Sydney, NSW 2006, Australia

<sup>e</sup> Electrochemistry and Materials Group, Department of Chemistry, K. L. E. Institute of Technology, Gokul, Hubballi-580030, Affiliated to Visvesvaraya Technological University, Karnataka, India

<sup>f</sup> Department of Chemistry and Biochemistry, Lamar University, Beaumont, Texas 77710, USA

<sup>g</sup> SET's College of Pharmacy, Dharwad, Karnataka, 580002 India

## ARTICLE INFO

### Keywords:

Core-shell structure  
Shell thickness  
Hydrogen production  
Sulphide wastewater  
Inorganic sacrificial agent  
Apparent  
Quantum efficiency

## ABSTRACT

This study focuses on the synthesis of Cu<sub>2</sub>S particles as the core wrapped-up with thin layer of TiO<sub>2</sub>-shell for improved surface and interface control of photo-excitons for H<sub>2</sub> production. Chemical states of metal Cu<sup>+</sup>, Ti<sup>4+</sup> ions were confirmed by X-ray Photo-electron and Electron Paramagnetic Resonance (g-factor of 2.03) Spectroscopy. Transmission Electron Microscopic images revealed the hexagonal shape of Cu<sub>2</sub>S wrapped-up with TiO<sub>2</sub> having the shell thickness varying from 12.0 to 16.7 nm. Time resolved transient photoluminescence decay spectra confirmed that three folds prolonged life-time of excitons generated on Cu<sub>2</sub>S@TiO<sub>2</sub> core-shell than pristine Cu<sub>2</sub>S. The batch photo-reactor used to evaluate the performance of photocatalysts in an aqueous solution containing Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>4</sub> promoted oxidation reaction for H<sup>+</sup> generation. The control over shell thickness directly influenced the optical and surface-interface properties, resulting in the enhanced H<sub>2</sub> production of 41.6 mmol h<sup>-1</sup> g<sup>-1</sup> of catalyst for an optimized catalyst with UV-vis light to H<sub>2</sub> production efficiency of 10.3%. The same catalyst also exhibited excellent stability for un-interrupted H<sub>2</sub> production upto 30 h, along with good results on recyclability and reusable efficiency. Scale-up operation performed to recover H<sub>2</sub> from sulphide wastewater in tank photo-reactor triggered H<sub>2</sub> gas 16.1 mmol h<sup>-1</sup> g<sup>-1</sup> of catalyst.

## 1. Introduction

Hydrogen (H<sub>2</sub>) fuel production via photocatalytic process by utilizing solar light is considered as a simple, sustainable and renewable route. This process often works well under ambient conditions and produces H<sub>2</sub> via detoxifying industrial wastewater, which ensures the environmental cleaning and energy production is a novel approach to reform industrial waste [1,2]. Sulfide ions present in industrial wastes either as S<sup>2-</sup> or hydrogen sulfide (H<sub>2</sub>S) are toxic having an unpleasant odor. Petrochemical industry releases H<sub>2</sub>S containing (15–20%) wastewater as a by-product, and their treatment process produces elemental sulfur. Also, sewage treatment plant releases the wastewater

containing sulphide ion with concentration greater than 1200 mg/L. At present a large amount of energy being spent for this treatment, whereas photocatalytic process can be effectively utilized to recover H<sub>2</sub> gas [3,4].

The H<sub>2</sub> generation can be obtained using a variety of nanohybrid materials such as those including, but not limited to semiconductor metal chalcogenides [5–7]. And also a few reports on N-doped metal oxides, metal chalcogenides [7–11], noble metals as co-catalyst as well as core-shell co-catalyst [12–15], transition metal oxides [16–18], mixed metal oxides [19,20], metals as a co-catalyst [21,22], bimetallic quantum dot nanocomposites [23,24], transition metal chalcogenides [25,26]. A variety of metal oxides have also been used for H<sub>2</sub>S splitting

\* Corresponding author at: SET's College of Pharmacy, Dharwad, Karnataka, 580002 India.

\*\* Corresponding authors.

E-mail addresses: [vpreethi@hindustanuniv.ac.in](mailto:vpreethi@hindustanuniv.ac.in) (V. Preethi), [aminabhavit@gmail.com](mailto:aminabhavit@gmail.com) (T.M. Aminabhavi), [shankar@yogivemanauniversity.ac.in](mailto:shankar@yogivemanauniversity.ac.in) (M.V. Shankar).

such as noble metal and metal oxides [27,28], and metal and metal oxides/sulphides [29]. However, their efficiency is still low to claim for large-scale applications. Recently our group reported, metal chalcogenide based core-shell type photocatalysts have attracted much interest to improve efficiency and suppressed the photo-corrosion [30–32]. Especially,  $\text{Cu}_2\text{S}$  based core-shell materials are attractive in view of their tunable optical and catalytic properties.

Copper is an earth-abundant material and  $\text{Cu}_2\text{S}$  synthesized by using simple chemical method having better semiconducting properties to absorb solar light and hence it is potential material for photocatalytic  $\text{H}_2$  generation. It was explained that  $\text{Cu}_2\text{S}$  have narrow band gap from 1.8 to 2.4 eV, have the potential to absorb visible spectrum of solar light and generated excitons have required potential for oxidation and reduction reactions [33,34]. All these attributes favor  $\text{Cu}_2\text{S}$  to be a potential photocatalyst for  $\text{H}_2$  production, but photo-corrosion in  $\text{Cu}_2\text{S}$  is a bottle-neck to scale-up. Hence, construction of core-shell type materials is considered to be a viable opportunity to overcome these issues. Titanium is a well-known UV light active photocatalyst with exceptional properties such as non-toxicity, low cost, low infrared absorption, good photo-stability, transparency under UV–vis light, suitable band edge potential and catalytic active sites [35]. It is considered as one of the promising materials for the photocatalytic splitting of water into  $\text{O}_2$  and  $\text{H}_2$  gases [36]. It is expected that the combination of the two best photocatalysts ( $\text{Cu}_2\text{S}$ ,  $\text{TiO}_2$ ) can be a suitable approach to improve the overall photocatalytic efficiency.

In the earlier literature, Park et al., reported  $\text{Cu}_2\text{S}$  spherical type nanostructures decorated with metal as a co-catalysts for  $\text{H}_2$  generation [37]. Kar et al., reported the synthesis and properties of  $\text{Cu}_2\text{S}$ ,  $\text{CuS}$  nanorods and nanowalls for  $\text{CO}_2$  photoreduction [38]. Low-thermal synthesis of  $\text{CuS}$  quantum dots decorated on  $\text{TiO}_2$  nanotube was also reported [39]. The role of co-catalyst in  $\text{CuS@TiO}_2$  core-shell structured particle has been studied [40].  $\text{CuS}$  nanorods, as well as nanowires, were synthesized by the simple chemical method by Poulomi Roy et al. [41]. Non noble-metal  $\text{CuS-CdS}$  nanocomposites were evaluated for photocatalytic  $\text{H}_2$  production [42].  $\text{Cu}_2\text{S}$  nanostructures with different morphologies such as 2-D hierarchical, nanobelts, nanorod, and nanowires were also reported [43–45]. To the best of our knowledge, no reports on  $\text{Cu}_2\text{S@TiO}_2$  based core-shell materials for photocatalytic  $\text{H}_2$  generation. Hence, in this study, we synthesize  $\text{Cu}_2\text{S@TiO}_2$  core-shell materials by a two-stage method using structure-directing agent, resulting in uniformly coated core-shell nanostructures with a shell thickness of few nanometres. Experimental parameters were fine-tuned to attain higher catalytic activity of  $41.6 \text{ mmol h}^{-1} \text{ g}^{-1}$  of catalyst besides continuous  $\text{H}_2$  generation (time-on-stream) for 30 h. The optimized catalyst used in tank photo-reactor to recover  $\text{H}_2$  gas from sulphide containing wastewater and showed enhanced  $\text{H}_2$  generation rate of  $16.1 \text{ mmol h}^{-1} \text{ g}^{-1}$  of catalyst.

## 2. Experimental section

### 2.1. Design and synthesis of core-shell photocatalyst

A simple two-step process was designed for synthesis of hierarchical core-shell morphology of  $\text{Cu}_2\text{S@TiO}_2$  photocatalyst. At first, core material containing  $\text{Cu}_2\text{S}$  particle was prepared using structure-directing agent and followed by hydrothermal treatment.

#### 2.1.1. Preparation of $\text{Cu}_2\text{S}$ particles

Hydrothermal method and parameters were adopted from recent report [44]. Herein, 1:2 mol ratio of copper chloride di-hydrate (2.72 g, 0.53 M) and thiourea (2.43 g, 1.06 M) were sequentially added into ethylene diamine (30 mL) under magnetic stirring (15 min) at  $30 \pm 2^\circ\text{C}$ . The resulting mixture ( $\text{pH} = 13.5 \pm 0.2$ ) was packed and sealed in an autoclave and heated in electric oven at  $180^\circ\text{C}$  for 6 h. Thus the precipitate was collected via centrifugation and subjected to washing twice with distilled  $\text{H}_2\text{O}$  followed by  $\text{C}_2\text{H}_5\text{OH}$ . Finally, black

material was dried at  $80 \pm 2^\circ\text{C}$  for 12 h and labelled as  $\text{Cu}_2\text{S}$ . The same procedure was repeated few times to collect few grams of catalyst used for characterization and photocatalytic activity.

#### 2.1.2. Preparation of $\text{Cu}_2\text{S@TiO}_2$ core-shell morphology

A surface protection thin-layer of  $\text{TiO}_2$  on  $\text{Cu}_2\text{S}$  particles was achieved by following the experimental conditions reported in recent publication [46]. Typically, 1:0.3 M ratios of  $\text{Cu}_2\text{S}$  particles (50 mg) and trisodium citrate dihydrate (200 mg) was sequentially added into 50 mL of iso-propanol subjected to sonication for 30 min at  $30 \pm 2^\circ\text{C}$ . An amount of  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  (TTIP, 0.42 mL) solution was drop-wise added into the above suspension containing  $\text{Cu}_2\text{S}$ , followed by drop-wise addition of deionized  $\text{H}_2\text{O}$  (30 mL) and stirring continued for 2 h at  $30 \pm 2^\circ\text{C}$ . The above mixture was transferred and sealed in an autoclave, which then heated at  $180 \pm 2^\circ\text{C}$  for 15 h. The black product washed twice in deionized  $\text{H}_2\text{O}$  followed by  $\text{C}_2\text{H}_5\text{OH}$ , centrifuged to separate the solid and dried at  $80 \pm 2^\circ\text{C}$  for 12 h. In order to study the effect of shell thickness ( $\text{TiO}_2$ ) the concentration of TTIP varied from 0.14, 0.28, 0.42, 0.59 and 0.74 mL (0.01M to 0.08M) which are labelled as CST-1, CST-2, CST-3, CST-4 and CST-5 respectively. The same procedure was repeated few times to collect few grams of catalyst used for characterization and photocatalytic activity.

### 2.2. Photocatalytic hydrogen production

#### 2.2.1. Batch photo-reactor

The detailed experimental procedure is elaborated in recent report [31]. In brief, known amount of chosen photocatalyst was dispersed into aqueous solution of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_4$  (0.3 M, 50 mL) kept in single port quartz photo-reactor (190 mL). The reactor port was tightly sealed with rubber septum and the contents were subjected to adsorption and nitrogen gas purging results in inert conditions. A solar simulator (Xe lamp = 260 W, Oriel Instruments, Newport Cooperation, USA) fitted with infra-red filter used to carryout photocatalytic experiments. The entire set-up kept in air-conditioned facility and maintained experimental temperature of  $25 \pm 2^\circ\text{C}$ . At periodic interval of one hour, gas samples withdrawn using gas syringe from the photo-reactor injected into gas chromatograph (Shimadzu Gas Chromatograph-2014) fitted with a thermal conductivity detector. All the gas samples were analysed at identical experimental conditions.

#### 2.2.2. Tank photo-reactor

Fig. 1 shows the photographic image of square shaped tank photo-reactor (capacity 5 L) made-up of acrylic plastic used in the present experimental work. Reactor consists of two cylindrical type tubes, the first one used for  $\text{N}_2$  gas purging, and other one used to collect the  $\text{H}_2$  gas generated through photocatalytic process. The sulphide wastewater collected from biogas scrubbing unit, a sewage treatment plant (STP) and its sulphide concentration (1280 mg/L) was analyzed by the standard iodometric method. Prior to solar light irradiation, the reactor purged with  $\text{N}_2$  gas for 45 min to ensure the inert atmosphere and adsorption under dark condition. The generated  $\text{H}_2$  gas was quantified by water displacement method using inverted measuring cylinder. The photocatalytic experiments were carried out under solar light irradiation at Padur, Chennai, India (location  $12.48^\circ\text{N}$   $80.13^\circ\text{E}$ ) the light intensity was measured every hours using a Lux meter (Model: LX 101A) between 10.00 a.m. to 2.00 pm and average light intensity is about 86,800 lx.

## 3. Results and discussion

### 3.1. Steps involved in synthesis of $\text{Cu}_2\text{S@TiO}_2$ core-shell

Fig. 2 illustrates the step-wise formation of  $\text{Cu}_2\text{S@TiO}_2$  core-shell by a facile double stage method. At first, preparation of  $\text{Cu}_2\text{S}$  core (i) Dissolution of copper precursor in ethylene diamine solution (served as

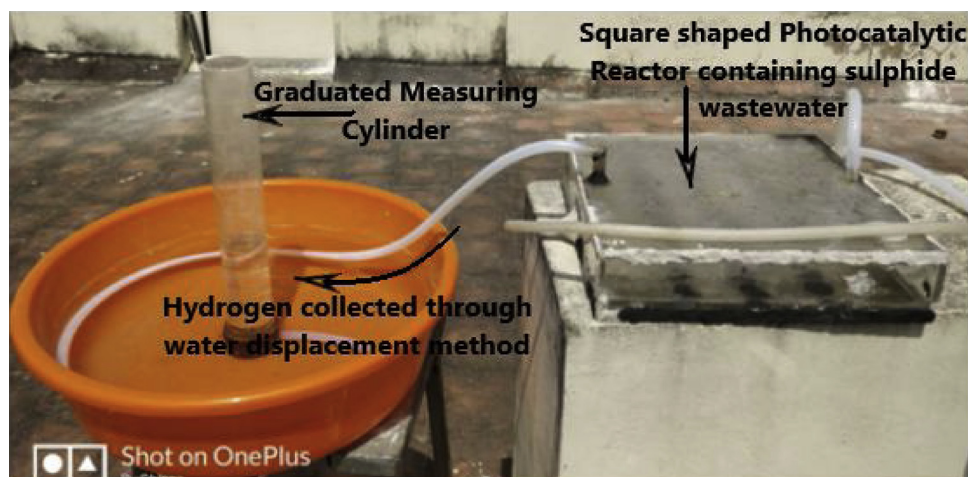


Fig. 1. Experimental set-up for the photocatalytic recovery of  $H_2$  from  $H_2S$  containing industrial wastewater under solar light irradiation.

structure-directing agent) turns colourless into blue colour indicates copper ions attached to ethylene diamine (en) in the form of  $Cu(en)_2$ . (ii) Addition of thiourea results change of colour from blue to pale green due to formation of surface urea complex. (iii) Upon continuous magnetic stirring thus obtained black  $Cu_2S$  adsorbed with reaction by-products on hexagonal and spheroids morphologies. (iv) Hetero-structures of hexagonal and spheroids shapes with negative surface charge obtained. Secondly, preparation of thin-layer of  $TiO_2$  shell (v) a positive ion layer formed on  $Cu_2S$  particles by dispersion in tri-sodium citrate solution. (vi) TTIP hydrolyzed to form  $Ti(OH)_4$  anions in-turn adsorbed on positive layer of  $Cu_2S$  (vii) a thin-layer of  $TiO_2$  formed on  $Cu_2S$  besides adsorption of reaction by-products. (viii) dried material have clean surface of  $Cu_2S@TiO_2$  core-shell structure.

### 3.2. Characterization of photocatalysts

#### 3.2.1. Structural and morphological analysis

Fig. 3 shows XRD pattern of pristine and core-shell photocatalysts with different  $TiO_2$  amount. The cuprous sulfide showed cubic crystal and chalcocite phases, that match with the standard JCPDS values. The  $2\theta$  values located at  $27.9$ ,  $29.4$ ,  $32.3$  and  $46.4^\circ$  are correlated with (100) (111), (200) and (220) planes of  $Cu_2S$  [44,48]. The peak at  $2\theta = 25.42^\circ$  indicates (101) plane of  $TiO_2$  anatase phase (JCPDS No: 21-1272) with tetragonal crystal structure. These values are in good agreement with  $Cu_2S@TiO_2$  core-shell nanocomposites [49,50]. In Fig. 3, one can see that with increasing the concentration of TTIP leads to increased  $TiO_2$  content onto the surface of the core ( $Cu_2S$ ), the peak intensities

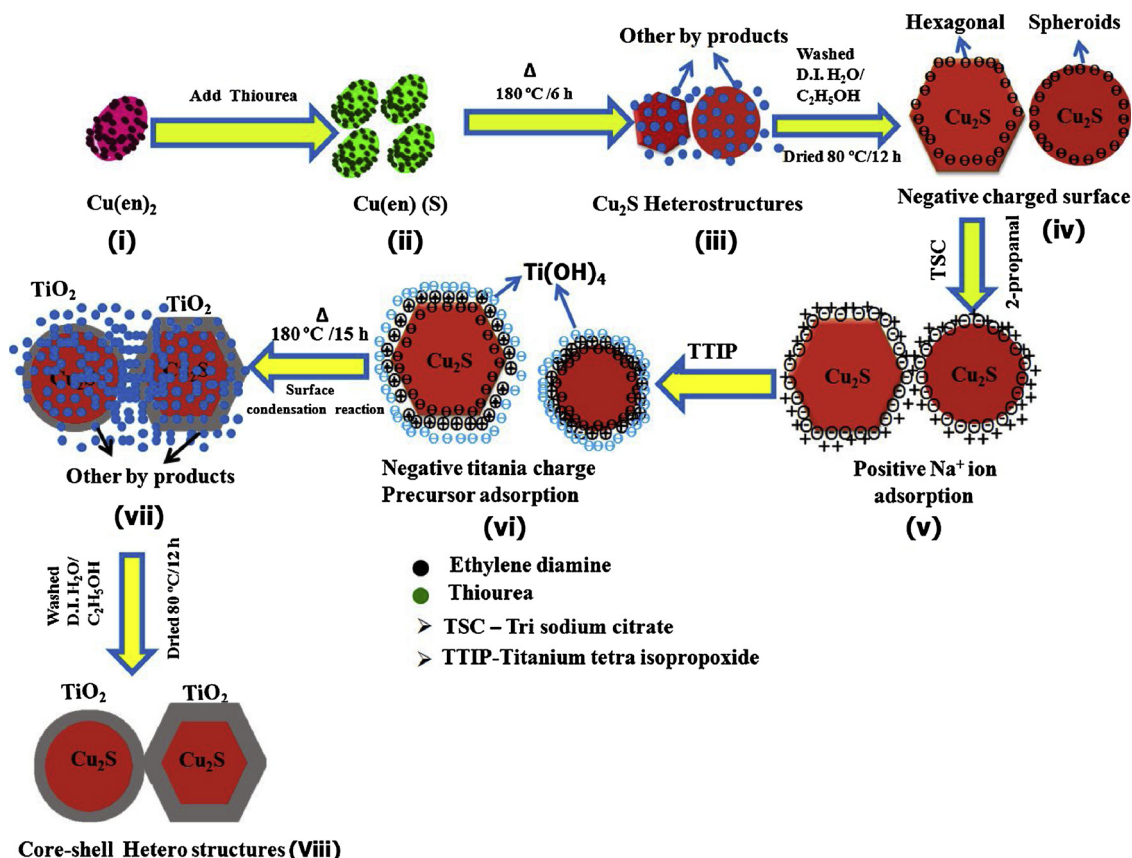


Fig. 2. Schematic illustration of  $Cu_2S@TiO_2$  core-shell nanostructures in two-step method.



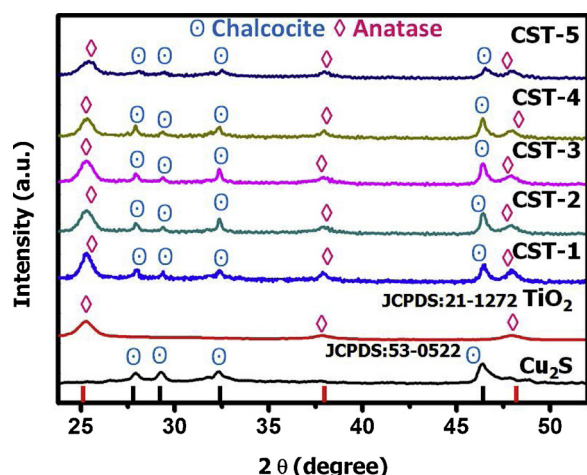


Fig. 3. XRD pattern of pristine and  $\text{Cu}_2\text{S}@ \text{TiO}_2$  core-shell photocatalysts.

decrease from CST-1 to CST-5 compared to the crystallinity of  $\text{TiO}_2$ . Recently, Li et al., [49] reported  $\text{Cu}_2\text{S}@ \text{ZnO}$  hetero nanostructures and explained about the crystal structure as well as phase. Xue et al., explained the crystal planes and phase corresponds to  $\text{Cu}_2\text{S}$  for Li-ion batteries [44]. Their result denotes that the synthesis time may also improve the purity and phase structure of the final core-shell structure.

FT-IR spectrum of CST-3, pristine  $\text{TiO}_2$  and  $\text{Cu}_2\text{S}$  photocatalysts displayed in Fig. FS1 show strong peaks at  $1085$  and  $1040\text{ cm}^{-1}$  that are assigned to stretching vibration of Cu-S in Ti-O group in  $\text{C}_2\text{H}_5\text{OH}$ . The peak at  $890\text{ cm}^{-1}$  assigned to Ti of CST-3, while peaks of pristine  $\text{Cu}_2\text{S}$  and  $\text{TiO}_2$  were well matched with stretching frequency values of CST-3 core-shell nanocomposites. The spectra of pristine  $\text{TiO}_2$ ,  $\text{Cu}_2\text{S}$  and CST-3 are consistent with standard spectra of  $\text{TiO}_2$  and  $\text{Cu}_2\text{S}$  [51,52]. The O–H stretching vibrations observed at  $3445\text{ cm}^{-1}$  indicate OH functional group present in  $\text{Cu}_2\text{S}@ \text{TiO}_2$  core-shell is ascribed to moisture present of the composite. Absorption at  $1626\text{ cm}^{-1}$  corresponds to  $\text{Cu}_2\text{S}$  stretching in S group, while a shoulder peak at  $1612\text{ cm}^{-1}$  is due to sulfur and double bond bending. The peak around  $1145 - 1350\text{ cm}^{-1}$  corresponds to oxygen and  $\text{Cu}^{+1}$  stretching, while those at  $632.5$  and  $634.5\text{ cm}^{-1}$  are assigned to  $\delta\text{-Ti}^{+4}$ . The above results show well separated and intense peaks confirming no impurities of the core-shell material [51,53,54].

Fig. 4 shows TEM images of  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{S}@ \text{TiO}_2$  core-shell (CST-2, CST-3 and CST-4) photocatalysts. Fig. 4(a) display hetero nanostructures predominantly with a hexagonal structure. The pristine  $\text{Cu}_2\text{S}$  has an average diameter of  $336\text{ nm}$  and core  $\text{Cu}_2\text{S}$  is protected by the nanoscale layer of anatase  $\text{TiO}_2$  uniform shell (Fig. 4 (b,c)). The structures have hexagonal nanosheet-like morphology with a length about  $603\text{ nm}$ . For the core, average diameter was  $331\text{ nm}$  and  $\text{TiO}_2$  shell thickness increased at higher mole concentration of  $\text{TiO}_2$  precursor. The shell thicknesses of CST-2, CST-3 and CST-4 are  $12.04$ ,  $13.2$ , and  $16.7\text{ nm}$ , respectively (shown in Fig. 4(c, d, f)). HR-TEM image of CST-3 catalysts displayed lattice fringe of  $d = 0.307\text{ Å}$ , suggesting the existence of (110) plane of  $\text{Cu}_2\text{S}$  and the coated shell layer showed existence of anatase  $\text{TiO}_2$  with  $d = 0.354\text{ Å}$  correspond to (101) plane (Fig. 3e). Fig. 3 (g) revealed the elemental composition of Ti (10%), Cu (46%), S(23%) and O (21%) in optimized CST-3 hierarchical nanocomposite (Fig. 4f). Further consolidated elemental mapping of the CST-3 core-shell photocatalyst shown in Fig. FS2(a). Fig. FS2(b–d) depicts mapping of individual elements copper, sulphur, titanium and oxygen and it confirms the uniform distribution in the photocatalyst.

### 3.2.2. Optical and surface properties of $\text{Cu}_2\text{S}@ \text{TiO}_2$ photocatalyst

The UV–vis spectrum of core-shell photocatalysts are displayed in Fig. 5. It shows two shoulder-peaks, of which one is assigned to UV-light absorption in the range of  $395\text{--}405\text{ nm}$  attributed to light absorption by

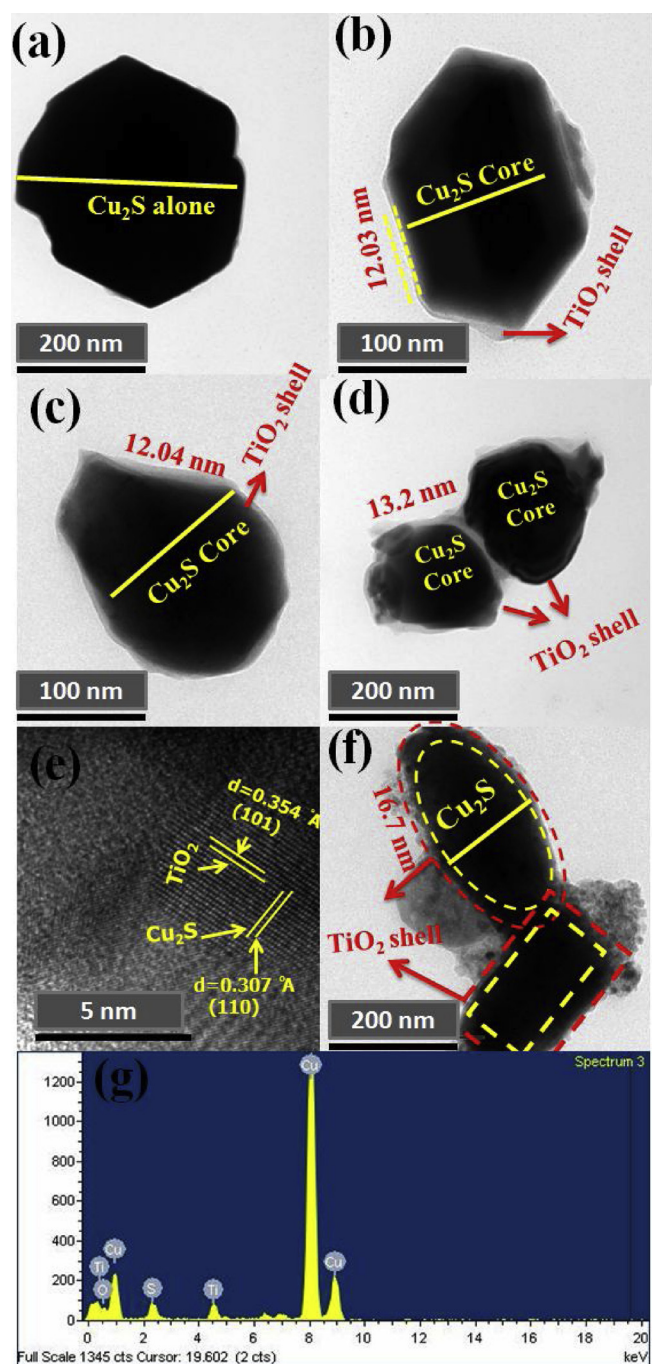


Fig. 4. HR-TEM images of  $\text{Cu}_2\text{S}@ \text{TiO}_2$  core-shell photocatalysts (a)  $\text{Cu}_2\text{S}$  hexagonal particle (b,c) Shell thickness of CST-2 (d) Shell thickness of CST-3 (e) SAED pattern of CST-3 (f) Shell thickness of CST-4 (g) EDAX of CST-3.

$\text{TiO}_2$ , while the second peak between  $550$  and  $555\text{ nm}$  assigned to  $\text{Cu}_2\text{S}$  core material which indicates cuprous sulfide allows visible light absorption region. The relative intensity of cuprous sulfide with respect to the core material decreases, however, the absorption edge shifted towards  $550\text{--}620\text{ nm}$  with increasing the amount of  $\text{TiO}_2$  from CST-1 to CST-5. The decrease in visible absorption spectrum is proportional to amount of  $\text{TiO}_2$  precursor that fetched thicker layer which contributes to reflection of irradiated light [55–57]. The absorption of  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{S}@ \text{TiO}_2$  catalysts around  $620\text{ nm}$  is ascribed to absorption of visible light by  $\text{Cu}_2\text{S}$  [58] while the core-shell catalyst absorbs both in UV–vis and visible light due to the combination of narrow ( $\text{Cu}_2\text{S}$ ) and wide band gap ( $\text{TiO}_2$ ) materials [59,60].

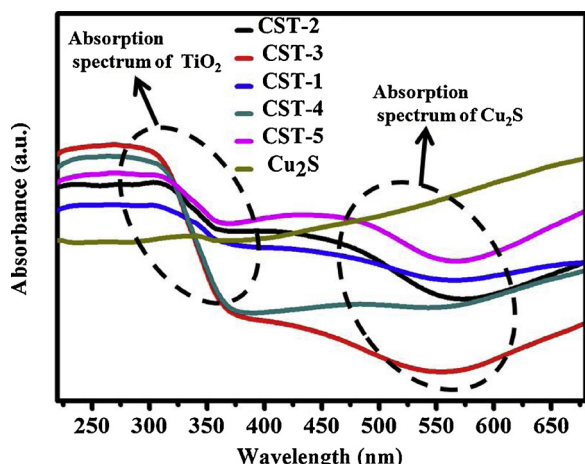


Fig. 5. DR UV-vis spectra of  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{S}@\text{TiO}_2$  core-shell photocatalysts.

Fig. 6 shows the X-ray photoelectron spectrum of CST-3. The Cu 2p peak in Fig. 6(a) shows two major peaks at 931.8 and 951.7 eV attributes to Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  and shake up peak are present in the core-shell composites which confirms copper exhibits +1 oxidation state. Fig. 6(b) displays S 2p spectrum, with major peaks at 161.8 and 160.6 eV, respectively that correspond to S  $2p_{1/2}$  and S  $2p_{3/2}$ , where sulfur exists as  $\text{S}^{2-}$ . The binding energy values of copper (Cu) and sulphur (S) are in good agreement with the earlier studies [25,61,62]. Fig. 6(c) depicts two peaks one at 457.3 and another at 463.3 eV that are attributed to  $2p_{3/2}$  and  $2p_{1/2}$  of Titanium exists  $\text{Ti}^{4+}$  state. The peaks at 528.4 and 530.5 eV corresponding to O 1s spectra reveal the existence of  $\text{O}^{2-}$  valence state (Fig. 6(d)). The binding energy values of

Ti, O, Cu and S in the optimized catalyst well matched with the standard values and are in their stable oxidation states and well correlate with the literature reports [63,64].

Electronic paramagnetic resonance spectroscopy (EPR) analysis provided information on the characteristic atomic state of the compositions and electronic structure of  $\text{Cu}_2\text{S}@\text{TiO}_2$  core-shell and pristine  $\text{Cu}_2\text{S}$  materials. Fig. 7 (a and b) shows EPR spectrum of  $\text{Cu}_2\text{S}@\text{TiO}_2$  and  $\text{Cu}_2\text{S}$  photocatalyst showed singlet signal and g-factor value of 2.03. The results are in good agreement with literature value and confirm that copper exists as +1 and titanium has +4 oxidation states in CST-3 photocatalyst [65,66].

### 3.2.3. Life-time studies of photo-excited

Fig. 8(a) displayed the photoluminescence (PL) spectra of pristine and core/shell photocatalysts. The experimental data on wavelength versus peak intensity shows that the peak intensity of CST-3 is significantly lower than  $\text{Cu}_2\text{S}$ . Under identical conditions, the peak intensity describes the recombination rate of photo-excited thus hierarchical structure in core/shell CST-3 showed lower rate of recombination [67]. In order to explore the life-time of photo-excited, time-resolved emission spectra were recorded at 428 nm for both catalysts and results as time versus peak intensity is displayed in Fig. 8(b). The emission decay kinetics for  $\text{Cu}_2\text{S}$  and CST-3 fitted single-exponentially with time constants ( $\tau$ ) 24.5 and 92.9 ps respectively. It is interesting to note that photo-excited in CST-3 have more than 3 folds prolonged life-time than  $\text{Cu}_2\text{S}$  alone. The spatial separation of electron and hole in excitons result in decrease of wave function overlap and thus a longer lifetime in type II heterostructures. As a result, increase in life-time of charge carriers in core-shell can be explained in two ways, an effective spatial separation of excitons via band bending from  $\text{Cu}_2\text{S}$  to  $\text{TiO}_2$  surface and secondly trapping at defects located at interface. Recent report on CdSe-ZnS core-shell quantum dots bonded cobalt

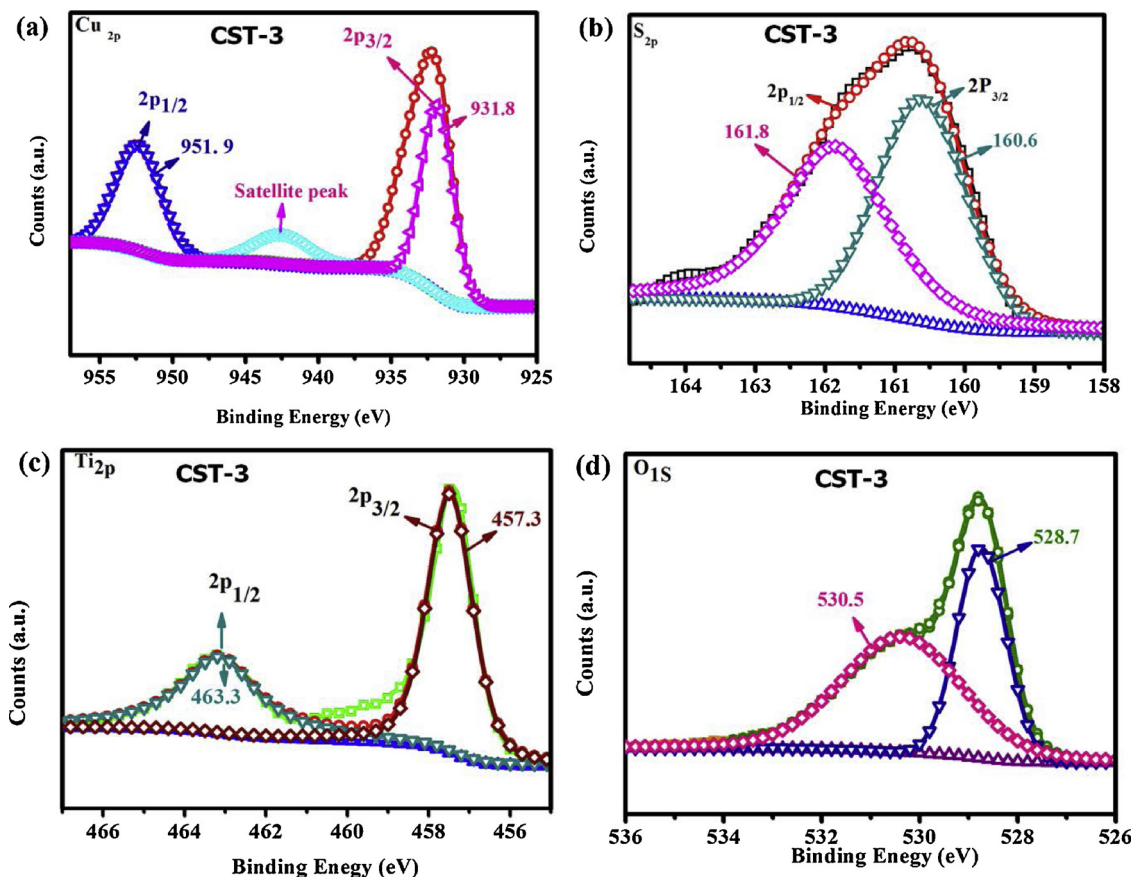


Fig. 6. X-ray photoelectron spectroscopy of CST-3 core-shell photocatalyst (a) Cu 2p (b) S 2p (c) Ti 2p (d) O 1s.

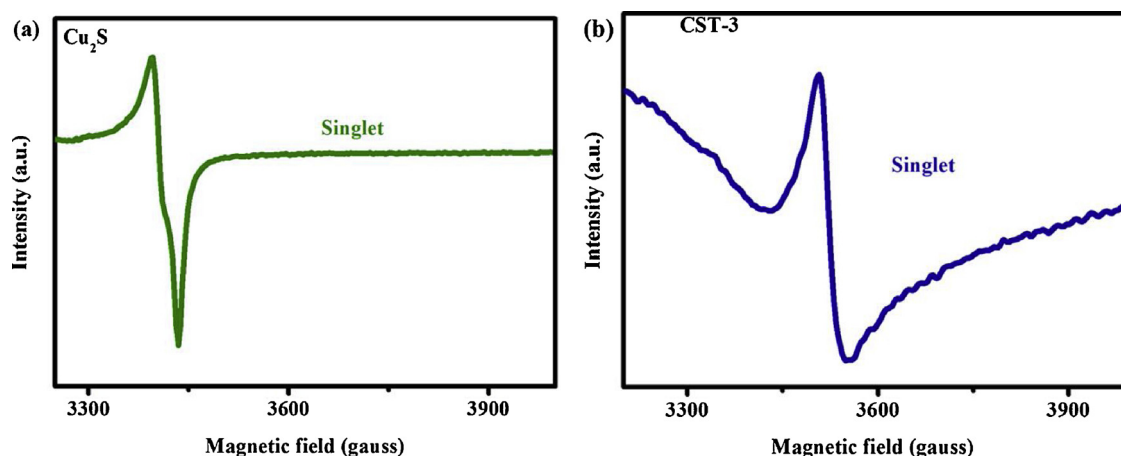


Fig. 7. Electronic spin resonance spectra of (a)  $\text{Cu}_2\text{S}$  (b) CST-3 core-shell photocatalysts.

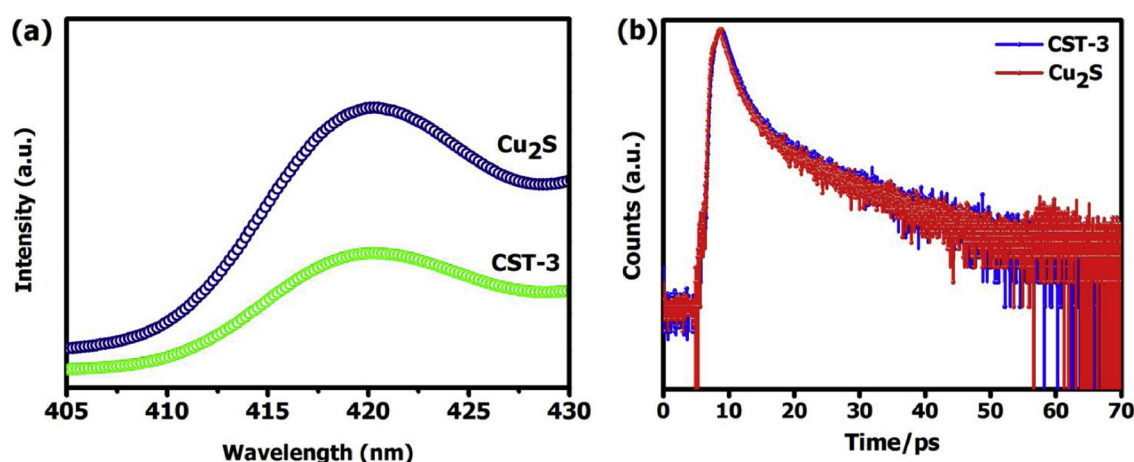


Fig. 8. (a) Photoluminescence decay spectra (b) Time resolved photoluminescence decay spectra of  $\text{Cu}_2\text{S}$  and CST-3 core-shell photocatalyst.

complexes at different concentration QD-C<sub>1</sub>, QD-C<sub>2</sub> and QD-C<sub>3</sub> showed a time resolved life time of 6.99–20.51 ns and 3.39 ns for pristine material [68]. Rawalekar et al. [69], elaborated prolonged life-time of charge carries in CdTe–CdS ( $\tau = 27.6$  ns) core-shell nanostructures than CdTe ( $\tau = 2.12$  ns).

### 3.3. Photocatalytic $\text{H}_2$ generation in batch reactor under simulated solar light irradiation

In core-shell type of photocatalysts, shell thickness plays predominant role for effective transmittance of light into semiconductor particle kept inside core available for photo-excitation process [32,70]. Similarly, exciton migrates from core to shell surface with life-time of few nanoseconds that involves in-situ redox reactions with molecules adsorbed at catalytic active sites. Hence, core protects the shell for direct contact with reaction medium. Often, core plays photo-sensitizer role and shell acts as catalyst/co-catalyst for surface reactions. In order to achieve improved  $\text{H}_2$  generation and photon utilization efficiency optimization of shell thickness as well as type of sacrificial agents are mandatory [23,71].

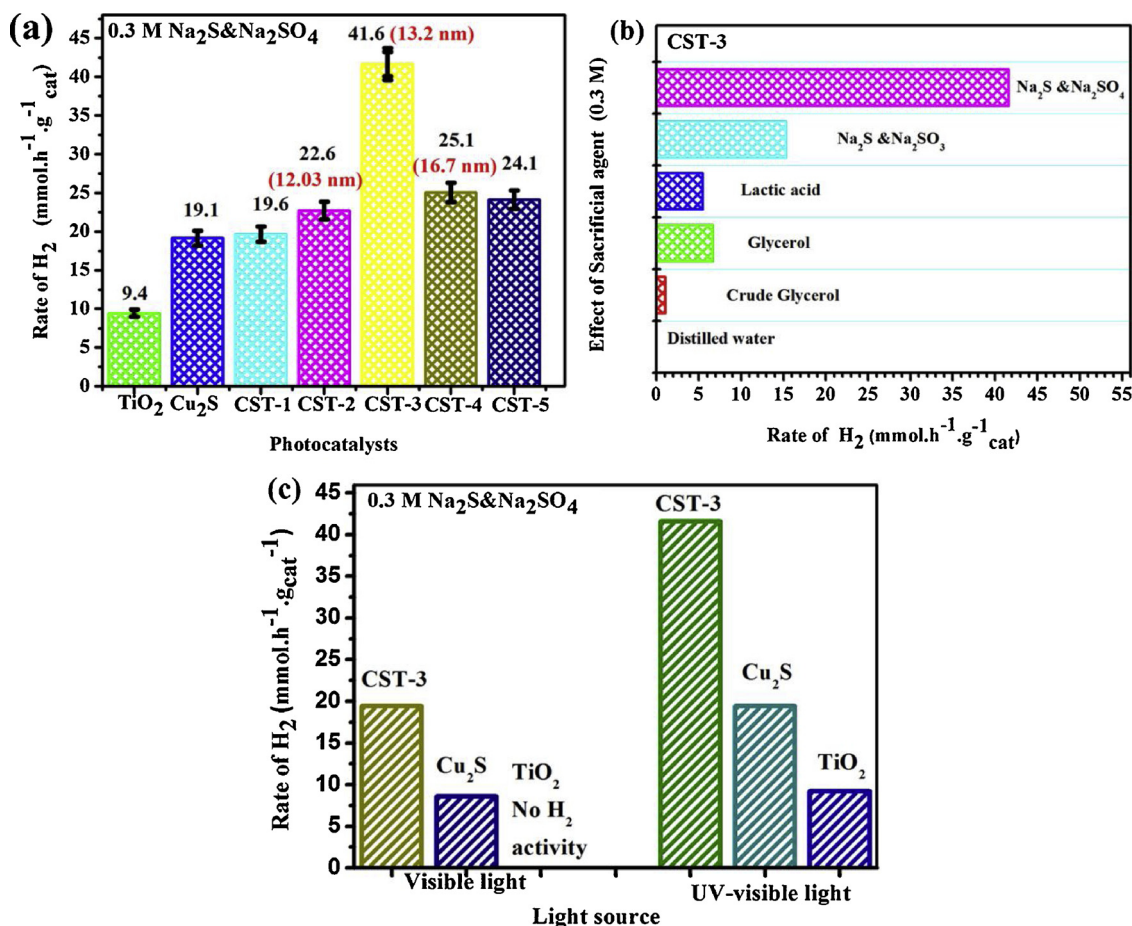
#### 3.3.1. Effect of $\text{TiO}_2$ shell thickness in $\text{Cu}_2\text{S}/\text{TiO}_2$ photocatalysts

Core-shell photocatalyst,  $\text{Cu}_2\text{S}/\text{TiO}_2$  with five different shell-thicknesses were studied for photocatalytic  $\text{H}_2$  generation with aqueous solution containing (0.3 M)  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_4$ . The experiments were carried out under simulated solar light irradiation for 4 h and the rate of  $\text{H}_2$  generation was calculated using standard formula for per hour and one gram catalyst. Fig. 9(a) displays rate of photocatalytic  $\text{H}_2$

generation by using core-shell with variable shell thickness and pristine catalysts in the following order CST-3 > CST-2 > CST-1 > CST-5 > CST-4 >  $\text{Cu}_2\text{S}$  >  $\text{TiO}_2$ . Among them, CST-3 shows highest rate of  $\text{H}_2$  generation i.e.  $41.6 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$  due to large number of photo-excitons utilized for oxidation reactions through hole ( $\text{h}^+$ ) with  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{O}$  to generate  $\text{H}^+$  ions, subsequently reduction of  $\text{H}^+$  with electrons ( $\text{e}^-$ ) to generate  $\text{H}_2$  gas. Further, at lower shell thickness light transmission to core is effective but photo-excitons recombination is predominant thus lower efficiency. Similarly, higher shell thicknesses opaque layer hinders intense of light penetration, results in lesser photo-excitons utilized for reaction. The poor performance of pristine  $\text{Cu}_2\text{S}$  and  $\text{TiO}_2$  is attributed to rate of photo-excitons recombination is faster than utilization [31,67,72]. These results are in-line with TEM images and UV–vis spectrum of photocatalysts (vide supra).

Domen et al. [67], investigated the effect of shell thickness on the core surface to conclude that shell thickness of 3–20 nm range is optimum for enhanced photocatalytic  $\text{H}_2$  production. Xu et al. [73], also reported metal@ $\text{TiO}_2$  (where metal = Au, Pd, and Pt) hierarchical nanohybrid with tunable ultrathin shell exhibited enhanced  $\text{H}_2$  production activity. Lakshmana Reddy et al. [32], reported superior photocatalytic  $\text{H}_2$  generation utilizing CdS/ZnS core-shell material and concluded that optimization of core diameter and shell thickness significantly affects the process efficiency. Recent report reveals that optimal shell thickness ( $\text{TiO}_2$  or NiO) in CdS/ $\text{TiO}_2$  and CdS/NiO core-shell photocatalyst accelerates the reaction efficiency besides inhibition of photo-corrosion [30,31].





**Fig. 9.** Photocatalytic activity of Cu<sub>2</sub>S@TiO<sub>2</sub> core-shell catalysts under UV-vis light irradiation. (a) optimization of TiO<sub>2</sub> (0.01M to 0.08M) concentration in shell thickness (b) effect of sacrificial agents (c) comparison of core-shell and pristine photocatalysts (CST-3, Cu<sub>2</sub>S, TiO<sub>2</sub>) under UV-vis light and visible light irradiation.

### 3.3.2. Effect of sacrificial reagents

A range of sacrificial agents such as alcohols, acids, amines, hydrocarbons and sulphur containing inorganic compounds were usually added at lower quantities into water to enhance the H<sup>+</sup> generation during oxidation reaction which is essential step for H<sub>2</sub> production as part of photocatalytic process [31,74]. Hence, in the present work, CST-3 photocatalyst evaluated with distilled water, equal molar concentration of alcohol, acid and two types of sulphur containing inorganic compounds. Fig. 9(b) shows rate of H<sub>2</sub> production against different sacrificial agents in the following order: Na<sub>2</sub>S&Na<sub>2</sub>SO<sub>4</sub> > Na<sub>2</sub>S&Na<sub>2</sub>SO<sub>3</sub> > Glycerol > Lactic acid > crude glycerol. The highest activity of Na<sub>2</sub>S&Na<sub>2</sub>SO<sub>4</sub> is ascribed to its higher electro negativity hence better adsorption on catalyst surface and effective oxidation of water into H<sup>+</sup> ions in-turn H<sub>2</sub> gas production. The lower performance of alcohol and acids are attributed to relatively poor adsorption and electron donating nature. The crude glycerol showed lowest performance due to mixture of lower and higher alcohols besides intermediates that have varied adsorption and electron donating nature that drastically affects the catalytic activity. The above results reveal that electron negativity of sacrificial agents facilitated *in-situ* generation of H<sup>+</sup> ions and suppress the charge carrier recombination. Lakshmana Reddy et al. [23,30], examined the effect of sacrificial agents such as primary, secondary and tertiary alcohols and found that glycerol having abundant –OH groups readily generated H<sup>+</sup> ions in aqueous solution using Cu/Ag-TiO<sub>2</sub> nanotubes as photocatalyst.

### 3.3.3. Effect of light source

The photocatalytic performance of tailor-made catalysts has been tested under different light sources viz., solar light, simulated solar

light/UV-vis light, visible light, monochromatic UV or vis light respectively [75]. In order to delineate the potential role of core (Cu<sub>2</sub>S) and shell (TiO<sub>2</sub>) in core-shell (Cu<sub>2</sub>S@TiO<sub>2</sub>) photocatalyst experiments were performed in aqueous solution of 0.3 M Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>4</sub> under light irradiation using solar simulator with UV cut-off filter (visible light) and no UV filter (UV-vis light). Fig. 9(c) shows photocatalytic H<sub>2</sub> generation using CST-3 (41.6 mmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>) and Cu<sub>2</sub>S (19.1 mmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>) under UV-vis light is about two folds higher than visible light irradiation. Whereas under visible light CST-3 (19.4 mmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>) and Cu<sub>2</sub>S (8.6 mmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>) displayed about two fold enhanced H<sub>2</sub> generation. In comparison with DR UV-vis spectra (vide supra), the higher activity of core-shell is attributed to Cu<sub>2</sub>S in core generated plenty of photo-excited electrons that can be activated under UV and visible spectrum instead of visible alone. On the other hand, pristine TiO<sub>2</sub> (band gap 3.2 eV) catalyst generated H<sub>2</sub> under UV-vis light and no activity under visible light due to large band gap that can generate excitons only under UV spectrum. In our recent studies, we have reported the synthesis of CdS-NiO and CdS-TiO<sub>2</sub> core-shell photocatalysts and compared their photocatalytic H<sub>2</sub> generation [30,31]. The hierarchical photocatalyst showed higher H<sub>2</sub> efficiency compared to pristine materials due to the presence of shell material that has protected the core from photo-corrosion and played a key role for enhanced H<sub>2</sub> production [69].

### 3.3.4. Time on stream, reusability and recyclability tests of Cu<sub>2</sub>S@TiO<sub>2</sub> photocatalyst

In order to explore the real-time potential of the efficient photocatalyst for H<sub>2</sub> generation, test has been conducted to evaluate its performance for prolonged time of utilization, repeated use with fresh

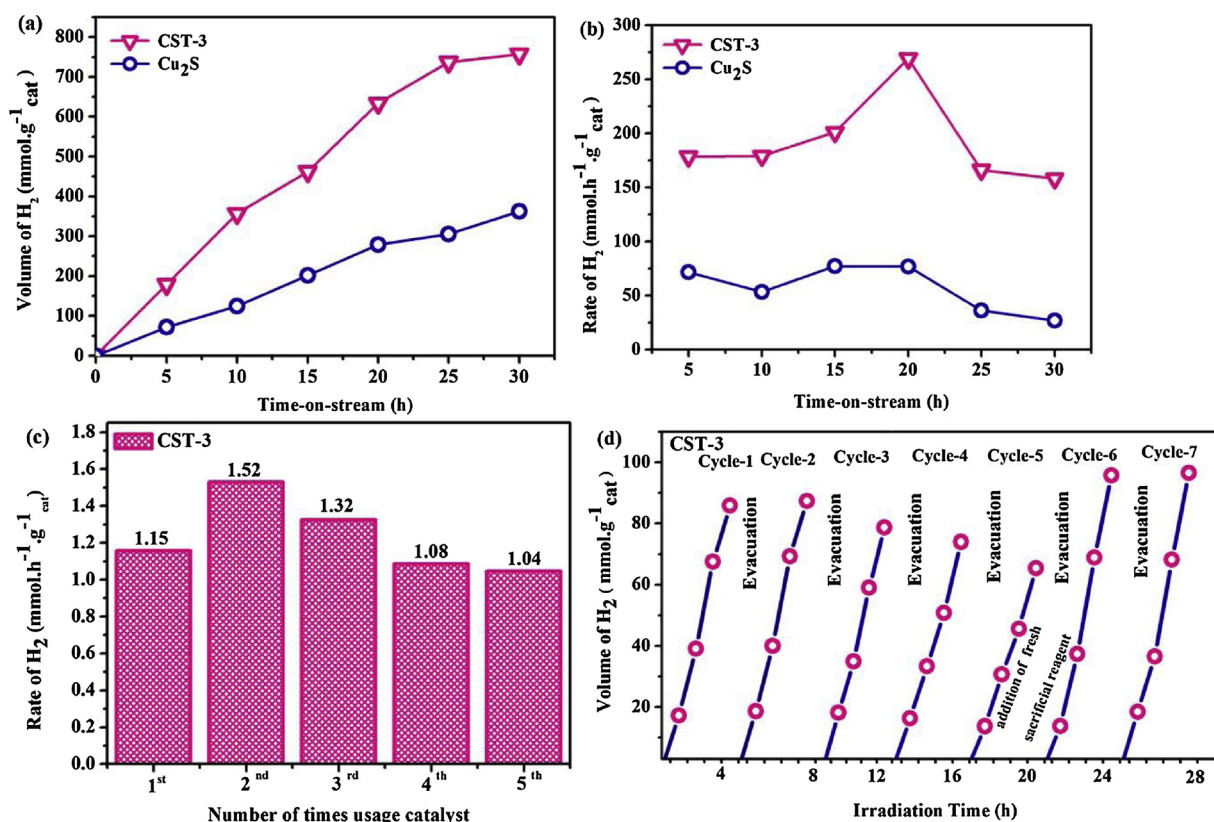


Fig. 10. Performance of CST-3 core-shell photocatalyst (a) Time-on-stream (b) stability (c) reusability (d) Recyclability.

reaction solution and batch experiments performed with same solution with evacuation of generated gas at periodic time intervals [76]. At first, time-on-stream studies were performed continuously for 30 h using pristine Cu<sub>2</sub>S and CST-3 dispersed in aqueous solution of 0.3 M Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>4</sub> under simulated solar light irradiation. Fig. 10(a) displays volume of H<sub>2</sub> generated at 5 h interval and found to increase with irradiation time. In Fig. 10(b) the rate of H<sub>2</sub> evolution linearly increased with time and shows highest value for 20 h and fall-down in activity of ~20% and then stabilize to the similar value for CST-3 catalyst. On the other hand, Cu<sub>2</sub>S catalyst displayed about 3 folds lower performance and slight decline in activity noticed for longer irradiation time. The increase in rate of H<sub>2</sub> production for CST-3 is attributed to stabilization of photocatalytic process under experimental conditions and effective release of H<sub>2</sub> gas from reaction medium. However, decline in activity is observed at 25 h and later is due to decrease in concentration of sacrificial agents as it undergoes irreversible oxidation and its intermediates may dramatically affect the catalytic process. The above results indicate that CST-3 exhibited excellent stability with time-on-stream performance for photocatalytic H<sub>2</sub> generation. Lakshmana Reddy et al. [32], explained the stability of core-shell CdS/ZnS photocatalyst under visible LED light for 100 h and 20 h for visible light irradiation. A slight decline in rate of H<sub>2</sub> production after prolonged usage attributed to concentration of sulphide and sulphate ions in reaction solution.

The catalyst reusability tests were carried out under optimized experimental conditions using CST-3 catalyst under simulated solar light irradiation. The catalyst was separated from reaction medium by centrifugation after 4 h of photocatalytic experiments and gas analysis. The separated catalyst was re-suspended into fresh sacrificial agent solution and performed experiments for another 4 h. The same procedure was repeated for 3 more times and rate of H<sub>2</sub> generation in each cycle is displayed in Fig. 10(c). The increase in catalytic performance observed in 2<sup>nd</sup> and 3<sup>rd</sup> cycles attributed to well stabilization of catalyst with sacrificial agents for physical adsorption process. Further, decrease and

stable activity in 4<sup>th</sup> and 5<sup>th</sup> cycle is observed due to partial masking of catalytic active sites by reaction intermediates. Similarly, MoS<sub>2</sub>, Au@MoS<sub>2</sub> and Au@MoS<sub>2</sub>-ZnO photocatalysts showed excellent stability for 8 reusability cycles [77].

The recyclability tests were executed for CST-3 under optimized conditions. At first cycle, fresh catalyst and reaction solution were subjected to light irradiation for 4 h and volume of H<sub>2</sub> generated was analyzed and quantified every one hour. In second cycle, the experimental set-up was used after careful evacuation and purged with nitrogen gas to simulate inert atmosphere. Similar procedure was repeated till 5<sup>th</sup> cycle, whereas fresh solution of 0.3 M sacrificial agent was added into the reactor, 6<sup>th</sup> and 7<sup>th</sup> cycle experiments were performed and generated gas was analysed and quantified as per the standard protocol (vide supra). Fig. 10 (d) displayed volume of H<sub>2</sub> generation using CST-3 catalyst and light irradiation period 4 h in each cycle and repeated for seven cycles. It is evident that slight decrease in activity during 3<sup>rd</sup>, 4<sup>th</sup> and 5<sup>th</sup> cycles attributed to decrease in concentration of sulphide and sulphate ions present in solution and regained in performance during 6<sup>th</sup> and 7<sup>th</sup> cycle is due to addition of fresh sacrificial agents. Recently Zhang et al. reports CdS/Titanate nanocomposite for seven cycles each cycle have 12 h continuous irradiation, it shows good stability [78].

Further, the crystal structure of the fresh and used catalyst was examined by XRD and results are depicted in Fig. 11. It shows that both have similar patterns confirming that CST-3 is highly stable. Further XPS analysis of used catalyst is shown in Fig. 12 (a,b,c and d). The experimental data well matched with fresh catalyst (Fig. 6) there is a slight shift in Ti spectra attributed to Ti-O and Ti-H<sub>2</sub>O in Cu<sub>2</sub>S@TiO<sub>2</sub> core-shell material. The above results strongly suggest that CST-3 is a stable photocatalyst.

The type of reactor, light source, volume of reaction solution, amount of catalyst etc varies from one laboratory to another. Hence, calculation of reaction efficiency as common parameter enable researchers to compare efficiency of different materials carried out in



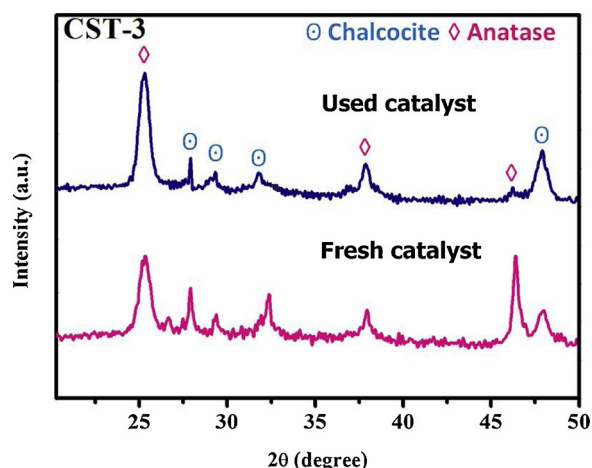


Fig. 11. XRD pattern of fresh and used CST-3 core-shell photocatalyst.

same or different labs. The UV–vis light to  $H_2$  energy conversion were calculated for pristine and the core-shell catalysts are listed in Table 1, where CST-3 showed higher UV–vis light to  $H_2$  conversion efficiency of 10.3% [69] (calculations details are given in the supporting information S3). In addition, quantum efficiency was calculated for CST-3, which is found to be 46.6% (for details see supplementary information S4), under solar light irradiation (1.5 G air mass filter with mean wavelength 768.6 nm) with the rate of  $H_2$  generation as  $227 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$ . Moreover, calculated the apparent quantum efficiency of CST-3 is 48.29% (see supplementary information) using air mass filter (1.5 G with mean wavelength 768.6 nm) under solar light irradiation, where the volume of  $H_2$  generation was  $771 \mu\text{mol g}_{\text{cat}}^{-1}$ . Zhukovskiy et al. [12],

Table 1

Comparison of photocatalyst for  $H_2$  production and UV–vis light to  $H_2$  conversion efficiency.

S. No.	Photocatalysts	$H_2$ generation ( $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$ )	UV–vis light <sup>a</sup> to $H_2$ production efficiency (%)
1	$\text{Cu}_2\text{S}$	19.1	4.8
2	$\text{TiO}_2$	9.2	2.27
3	CST -1	19.6	4.9
4	CST -2	22.6	5.6
5	<b>CST -3</b>	<b>41.6</b>	<b>10.3</b>
6	CST -4	25.1	6.2
7	CST -5	24.1	6.0

Bold values highlight maximum  $H_2$  generation ( $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$ ) & UV–vis light to  $H_2$  production efficiency (%).

<sup>a</sup> UV–vis light intensity =  $404 \text{ mW/cm}^2$ .

also calculated apparent quantum efficiency using the reported formula for Ni nanoparticles deposited CdS nanosheets and achieved high apparent quantum efficiency of 25%. Recently Xia et al. [79], reported  $\text{TiO}_2\text{-x/MCF}$  composite with a higher quantum yield 46% at 1.5 G air mass filter at the mean wavelength of 584.6 nm. Recently our research group reports developed CdS/ZnS core/shell photocatalyst for high quantum efficiency is 8.78% at 420 nm wavelength, also explained that optimization of shell thickness plays key a role for improvement photocatalytic  $H_2$  production [32].

#### 3.4. Photocatalytic $H_2$ generation in $H_2\text{S}$ containing wastewater in tank reactor

Photocatalytic  $H_2$  recovery studies were performed under direct natural sunlight irradiation using CST-3 catalyst. Fine tuning of

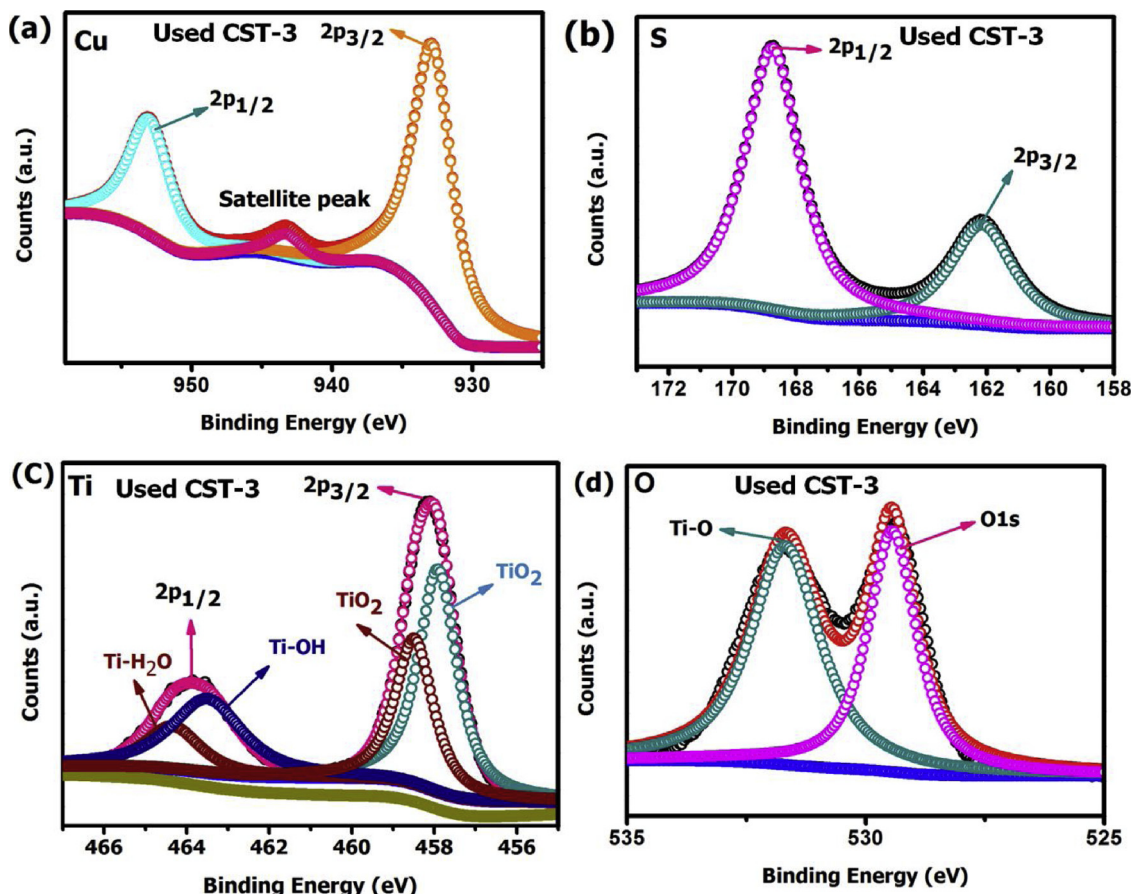


Fig. 12. X-ray photoelectron spectroscopy of used CST-3 catalyst (a) Cu 3d (b) S 2p (c) Ti 2p (d) O 1s.

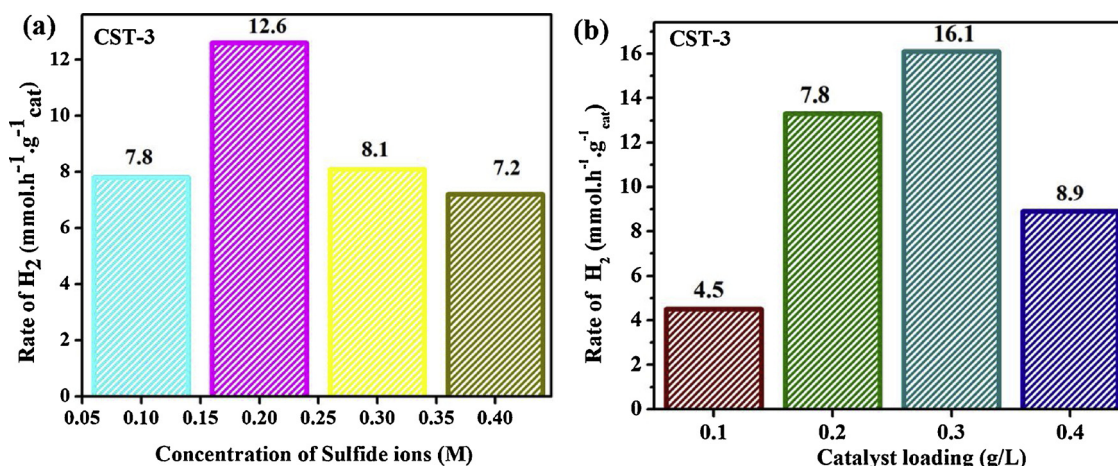


Fig. 13. Photocatalytic H<sub>2</sub> generation from H<sub>2</sub>S containing industrial wastewater in tank reactor (a) Effect of sulfite ion concentration (b) Effect of catalyst loading.

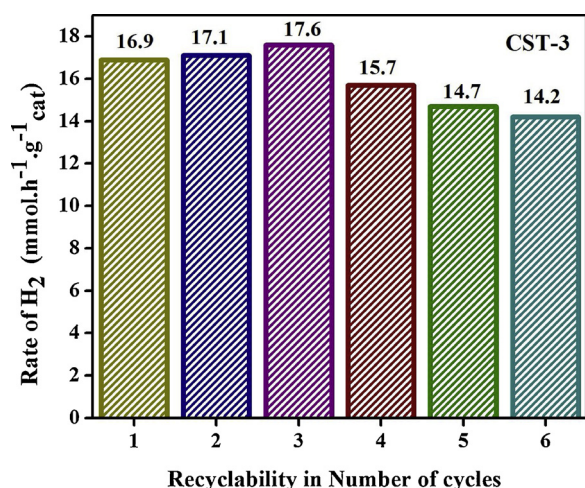


Fig. 14. Photocatalytic H<sub>2</sub> production of the CST-3 for six cycles.

parameters was carried out to optimize sulfite ion concentrations and catalyst loading for recovery of H<sub>2</sub> from an industrial sulfide containing wastewater. The optimized sulfite and catalyst loading was used for recyclability with six cycles.

#### 3.4.1. Effect of sulfite-ion concentration

The concentration of sulphide ion can vary in industrial effluent depends on the process parameters. Based on the experimental data on effect of Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>4</sub> concentration (vide supra), optimization of sulphide ion concentration is essential to achieve best photocatalytic performance. In the present work, effect of sulfite-ion concentration was studied from 0.1 to 0.4 M. The catalyst loading and average light irradiation used are 0.2 g/L and 1,113 W/m<sup>2</sup> (calculations available in supporting information S6) respectively. Fig. 13(a) shows the effect of sulfite ion concentration for recovering H<sub>2</sub> gas from the industrial sulfide wastewater. The highest H<sub>2</sub> recovery was found with 0.3 M sulfite ion concentration due to the maximum number of hole captured by CST-3 photocatalyst and the reaction solution was in close contact with catalyst surface. Several studies also stated that the smaller or higher amounts of sacrificial reagents may not possible to offer the maximum H<sub>2</sub> generation [47,80,81].

#### 3.4.2. Effect of catalyst loading

Fig. 13(b) shows the amount of catalyst loading for rate of photocatalytic H<sub>2</sub> generation from sulfide wastewater (H<sub>2</sub>S). The amount of catalyst loading was studied from 0.1 to 0.4 g/L. The highest H<sub>2</sub>

recovery was observed with 0.3 g/L of catalyst loading, ascribed to the abundant catalytic active sites formed on the surface of the CST-3 photocatalyst having better absorption-desorption properties [31,74]. The highest H<sub>2</sub> production was observed at an optimum catalyst loading of 0.3 g/L. It is observed that, at lower catalyst dosage, low catalytic activity is observed and it is proportional to active sites. On the other hand, above the optimum dosage, the opaque solution that significantly limits the light penetration to depth also scatters the photons leads to lower activity. Similar results were also been observed, Ruban et al. [82], reports catalyst loading concentration from 0.1 to 1 g/L amount this 0.5 g/L was optimized.

#### 3.4.3. Reusability of Cu<sub>2</sub>S@TiO<sub>2</sub> photocatalyst for sulphide wastewater treatment

Reusability tests were conducted using the optimized sulphite ion concentration (0.3 M), optimized catalyst dosage (0.3 g/L) with an average light irradiation of 127 W/m<sup>2</sup> (calculation shown in supporting information) for the recovery of H<sub>2</sub> from sulphide wastewater. Fig. 13 (a) shows the effect of sulphite ion concentrations on recovery of H<sub>2</sub> from sulphide wastewater. Among the difference concentration 0.2 M shows highest H<sub>2</sub> recovery from sulphide wastewater. Fig. 14 shows the reusability of TiO<sub>2</sub>/Cu<sub>2</sub>S catalyst for 6 cycles and the catalyst was active up to 5 cycles. Due to the core-shell structure, it showed minute charge carrier recombination protecting the core from photocorrosion, suggesting the capability of developed material is scalable for large-scale recovery of H<sub>2</sub> from sulphide wastewater.

#### 3.5. Reaction mechanism of Cu<sub>2</sub>S@TiO<sub>2</sub> core-shell photocatalyst

Based on the catalyst characterization data and photocatalytic experimental results, a plausible mechanism is projected for H<sub>2</sub> generation for pristine Cu<sub>2</sub>S and Cu<sub>2</sub>S@TiO<sub>2</sub> core-shell catalyst and displayed in Fig. 15. Based on the optical properties, it is explained that Cu<sub>2</sub>S generated photo-excited by absorbing light in UV-vis spectrum resulted major bulk/surface recombination besides photo-corrosion. Minor electron/hole at the surface involves in-situ oxidation and reduction reactions resulted in H<sub>2</sub> generation. On the other hand CST-3 having core/shell morphology effectively utilized excitons for generation of H<sup>+</sup> and its reduction to produce H<sub>2</sub> gas. Moreover, excitons recombination is suppressed greater extent and these results are matching with time resolved photoluminescence spectra. Butler et al., reported the reaction mechanism for enhanced photocatalytic activity towards water splitting using inorganic sacrificial agent solution in contact with the CdS/Pt nanohybrid material [83].



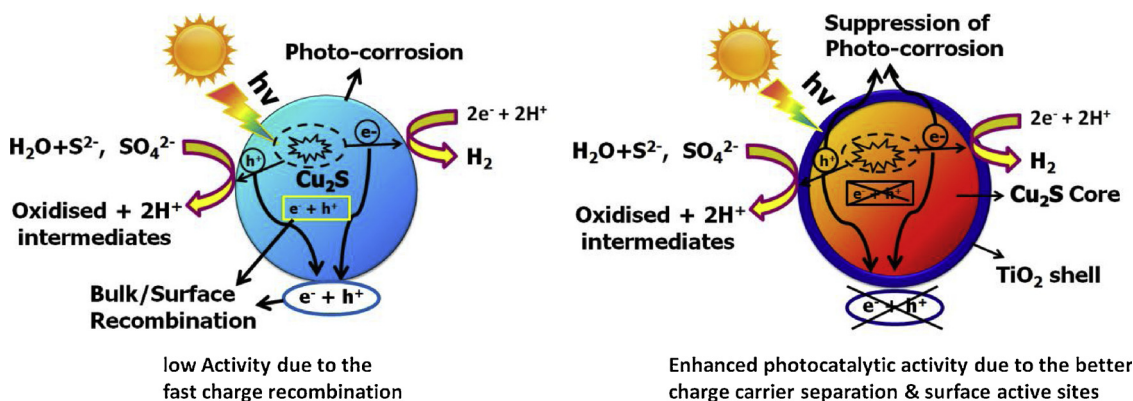


Fig. 15. Plausible reaction mechanism explaining charge carriers transformation from core to shell in  $\text{Cu}_2\text{S}@/\text{TiO}_2$  photocatalysts.

#### 4. Conclusions

The present study deals with the controlled synthesis of  $\text{Cu}_2\text{S}@/\text{TiO}_2$  hexagonal and spherical core-shell nanostructures by using structure-directing agent. XRD results confirm chalcocite phase of  $\text{Cu}_2\text{S}$  and anatase  $\text{TiO}_2$ . FT-IR revealed the formation of pure CST-3 core-shell nanocomposites via stretching frequencies observed at 632.4, 1628.4, 3445.4  $\text{cm}^{-1}$  corresponding to  $\text{Ti-O}$ ,  $\text{Cu}^{+1}$  and OH functional groups. TEM images revealed hexagonal nanostructured core-shell materials with shell thicknesses ranging from 12.03 to 16.7 nm. UV-vis spectra showed two broad absorption peaks at 450–480 and 500–600 nm, indicating its optical absorption property in the visible spectrum, while XPS and ESR chemical compositions revealed the existence of  $\text{Cu}^{+1}$  and  $\text{Ti}^{+4}$  states in  $\text{Cu}_2\text{S}$  and  $\text{TiO}_2$ , respectively. Time resolved photoluminescence decay spectra confirmed the prolonged life time of excitons in CST-3 than  $\text{Cu}_2\text{S}$  catalyst.

Photocatalytic  $\text{H}_2$  generation of 41.6  $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$  using CST-3 was 38% more than that of the  $\text{Cu}_2\text{S}$  core under simulated solar light irradiation. Besides the same catalyst proved stability for time-on-stream experiments. The CST-3 demonstrated a good recyclability for seven cycles and reusability for six cycles, suggesting its promise for practical applications. To the best of our knowledge, this is the first study to report the core-shell catalyst used in the treatment of industrial wastes for clean energy production over  $\text{Cu}_2\text{S}@/\text{TiO}_2$  core-shell photocatalyst. The enhanced  $\text{H}_2$  recovery rate of 16.1  $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$  was observed from sulphide wastewater. By fine-tuning of sulphite ion concentration and catalyst dosage, we could achieve good stability for six cycles with a high rate of  $\text{H}_2$  production (17.6  $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$ ) using  $\text{Cu}_2\text{S}@/\text{TiO}_2$  core-shell photocatalyst.

#### Acknowledgments

Financial support (Grant Application No.103/227/2014-NT) from Ministry of New and Renewable Energy (MNRE), India is gratefully acknowledged. Authors thankful to RUSA (YV University), MHRD, Govt. of India for providing infrastructural facilities.

#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.04.090>.

#### References

- [1] N.S. Chaudhari, A.P. Bhirud, R.S. Sonawane, L.K. Nikam, S.S. Warule, V.H. Rane, B.B. Kale, Green Chem. 13 (2011) 2500–2506, <https://doi.org/10.1039/c1gc15515f>.
- [2] A.P. Bhirud, S.D. Sathaye, R.P. Waichal, J.D. Ambekar, C.-J. Park, B.B. Kale, Nanoscale 7 (2015) 5023–5034, <https://doi.org/10.1039/C4NR06435F>.
- [3] V. Preethi, S. Kanmani, Int. J. Hydrogen Energy 37 (2012) 18740–18746, <https://doi.org/10.1016/j.ijhydene.2012.09.171>.
- [4] S.K. Apte, S.N. Garaje, G.P. Mane, A. Vinu, S.D. Naik, D.P. Amalnerkar, B.B. Kale, Small 7 (2011) 957–964, <https://doi.org/10.1002/smll.201002130>.
- [5] Y.P. Xie, Z.B. Yu, G. Liu, X.L. Ma, H.-M. Cheng, Energy Environ. Sci. 7 (2014) 1895–1901, <https://doi.org/10.1039/c3ee43750g>.
- [6] Y. Kang, Y. Gong, Z. Hu, Z. Li, Z. Qiu, X. Zhu, P.M. Ajayan, Z. Fang, Nanoscale 7 (2015) 4482–4488, <https://doi.org/10.1039/C4NR07303G>.
- [7] A.P. Bhirud, S.D. Sathaye, R.P. Waichal, L.K. Nikam, B.B. Kale, Green Chem. 14 (2012) 2790, <https://doi.org/10.1039/c2gc35519a>.
- [8] X. Wang, G. Sun, P. Routh, D.-H. Kim, W. Huang, P. Chen, Chem. Soc. Rev. 43 (2014) 7067–7098, <https://doi.org/10.1039/C4CS00141A>.
- [9] C. Sun, J. Zhang, J. Ma, P. Liu, D. Gao, K. Tao, D. Xue, J. Mater. Chem. A 4 (2016) 11234–11238, <https://doi.org/10.1039/C6TA04082A>.
- [10] S. Zhang, X. Yu, F. Yan, C. Li, X. Zhang, Y. Chen, J. Mater. Chem. A 4 (2016) 12046–12053, <https://doi.org/10.1039/C6TA04365H>.
- [11] D. Praveen Kumar, N. Lakshmana Reddy, M. Mamatha Kumari, B. Srinivas, V. Durga Kumari, B. Sreedhar, V. Roddatis, O. Bondarchuk, M. Karthik, B. Neppolian, M.V. Shankar, Sol. Energy Mater. Sol. Cells 136 (2015) 157–166, <https://doi.org/10.1016/j.solmat.2015.01.009>.
- [12] M. Zhukovskiy, P. Tongying, H. Yashan, Y. Wang, M. Kuno, ACS Catal. 5 (2015) 6615–6623, <https://doi.org/10.1021/acscatal.5b01812>.
- [13] Z. Zhang, M. Baek, H. Song, K. Yong, Nanoscale 9 (2017) 5342–5351, <https://doi.org/10.1039/C7NR00336F>.
- [14] K. Maeda, K. Teramura, D. Lu, N. Saito, Y. Inoue, K. Domen, Angewandte Chemie – Int. Edit. 45 (2006) 7806–7809, <https://doi.org/10.1002/anie.200602473>.
- [15] A. Tanaka, K. Teramura, S. Hosokawa, H. Kominami, T. Tanaka, Chem. Sci. 8 (2017) 2574–2580, <https://doi.org/10.1039/C6SC05135A>.
- [16] M.A. Rahman, S. Bazargan, S. Srivastava, X. Wang, M. Abd-Allah, J.P. Thomas, N.F. Heinig, D. Pradhan, K.T. Leung, Energy Environ. Sci. 8 (2015) 3363–3373, <https://doi.org/10.1039/C5EE01615K>.
- [17] R. Li, Y. Weng, X. Zhou, X. Wang, Y. Mi, R. Chong, H. Han, C. Li, Energy Environ. Sci. 8 (2015) 2377–2382, <https://doi.org/10.1039/C5EE01398D>.
- [18] K. Maeda, A. Xiong, T. Yoshinaga, T. Ikeda, N. Sakamoto, T. Hisatomi, M. Takashima, D. Lu, M. Kanehara, T. Setoyama, T. Teranishi, K. Domen, Angew. Chemie 122 (2010) 4190–4193, <https://doi.org/10.1002/ange.201001259>.
- [19] J. Zhang, Z. Liu, Z. Liu, ACS Appl. Mater. Interfaces 8 (2016) 9684–9691, <https://doi.org/10.1021/acsami.6b00429>.
- [20] J.-M. Li, H.-Y. Cheng, Y.-H. Chiu, Y.-J. Hsu, Nanoscale 8 (2016) 15720–15729, <https://doi.org/10.1039/C6NR05605A>.
- [21] Z. Li, Z. Zhang, Nanoresearch 11 (2017) 1530–1540, <https://doi.org/10.1007/s12274-017-1769-y>.
- [22] J. Warnan, J. Willkomm, J.N. Ng, R. Godin, S. Prantl, J.R. Durrant, E. Reisner, Chem. Sci. 8 (2017) 3070–3079, <https://doi.org/10.1039/C6SC05219C>.
- [23] N.L. Reddy, S. Kumar, V. Krishnan, M. Sathish, M.V. Shankar, J. Catal. 350 (2017) 226–239, <https://doi.org/10.1016/j.jcat.2017.02.032>.
- [24] A. Gallo, M. Marelli, R. Psaro, V. Gombac, T. Montini, P. Fornasiero, R. Pievo, V.D. Santo, Green Chem. 14 (2012) 330–333, <https://doi.org/10.1039/C2GC16112E>.
- [25] B. Liu, Z. Jin, L. Bai, J. Liang, Q. Zhang, N. Wang, C. Liu, C. Wei, Y. Zhao, X. Zhang, J. Mater. Chem. A 4 (2016) 14204–14212, <https://doi.org/10.1039/C6TA04789K>.
- [26] G. Yang, W. Yan, Q. Zhang, S. Shen, S. Ding, Nanoscale 24 (2013) 12432–12439, <https://doi.org/10.1039/c3nr03462c>.
- [27] H. Wender, R.V. Gonçalves, C.S.B. Dias, M.J.M. Zapata, L.F. Zagonel, E.C. Mendonça, S.R. Teixeira, F. Garcia, Nanoscale 5 (2013) 9310–9316, <https://doi.org/10.1039/c3nr02195e>.
- [28] S.A. Mahapure, P.K. Palei, L.K. Nikam, R.P. Panmand, J.D. Ambekar, S.K. Apte, B.B. Kale, J. Mater. Chem. A 1 (2013) 12835–12840, <https://doi.org/10.1039/c3ta12883k>.
- [29] S.K. Apte, S.N. Garaje, M. Valant, B.B. Kale, Green Chem. 14 (2012) 1455–1462, <https://doi.org/10.1039/c2gc16416g>.
- [30] N.L. Reddy, V.N. Rao, M.M. Kumari, P. Ravi, M. Sathish, M.V. Shankar, Mater. Res. Bull. 101 (2018) 223–231, <https://doi.org/10.1016/j.materresbull.2018.01.043>.
- [31] V.N. Rao, N.L. Reddy, M.M. Kumari, P. Ravi, M. Sathish, B. Neppolian, M.V. Shankar, Mater. Res. Bull. 103 (2018) 122–132, <https://doi.org/10.1016/j.materresbull.2018.01.043>.



- materresbull.2018.03.030.
- [32] N.L. Reddy, V.N. Rao, M.M. Kumari, M. Sathish, S. Muthukonda Venkatakrishnan, *Int. J. Hydrogen Energy* 43 (2018) 22315–22328, <https://doi.org/10.1016/j.ijhydene.2018.10.054>.
  - [33] M. Patil, D. Sharma, A. Dive, S. Mahajan, R. Sharma, *Procedia Manuf.* 20 (2018) 505–508, <https://doi.org/10.1016/J.PROMFG.2018.02.075>.
  - [34] R.J. Vimal Michael, J. Theerthagiri, J. Madhavan, M.J. Umapathy, P.T. Manoharan, *RSC Adv.* 5 (2015) 30175–30186, <https://doi.org/10.1039/C5RA03621F>.
  - [35] L. Sang, Y. Zhao, C. Burda, *Chem. Rev.* 114 (2014) 9283–9318, <https://doi.org/10.1021/cr400629p>.
  - [36] C. Wu, L. Lei, X. Zhu, J. Yang, Y. Xie, *Small* 3 (2007) 1518–1522, <https://doi.org/10.1002/sml.200700179>.
  - [37] J.-H. Park, P. Ramasamy, S. Kim, Y.K. Kim, V. Ahilan, S. Shanmugam, J.-S. Lee, *Chem. Commun.* 53 (2017) 3277–3280, <https://doi.org/10.1039/C7CC00071E>.
  - [38] P. Kar, S. Farsinezhad, X. Zhang, K. Shankar, *Nanoscale* 6 (2014) 14305–14318, <https://doi.org/10.1039/C4NR05371K>.
  - [39] C. Ratanatawanate, A. Bui, K. Vu, K.J. Balkus, *J. Phys. Chem.* 14 (2011) 6175–6180.
  - [40] Y. Zhou, Y. Lei, D. Wang, C. Chen, Q. Peng, Y. Li, *Chem. Commun. (Camb.)* 51 (2015) 13305–13308, <https://doi.org/10.1039/C5CC05156H>.
  - [41] P. Roy, S.K. Srivastava, *Mater. Lett.* 61 (2007) 1693–1697, <https://doi.org/10.1016/j.matlet.2006.07.101>.
  - [42] X. Deng, C. Wang, H. Yang, M. Shao, S. Zhang, X. Wang, M. Ding, J. Huang, X. Xu, *Sci. Rep.* 7 (2017) 32–36, <https://doi.org/10.1038/s41598-017-04270-y>.
  - [43] H.T. Zhang, G. Wu, X.H. Chen, *Langmuir* 21 (2005) 4281–4282, <https://doi.org/10.1021/la050741j>.
  - [44] X. Li, X. He, C. Shi, B. Liu, Y. Zhang, S. Wu, Z. Zhu, *Chemosuschem* 12 (2014) 3328–3333, <https://doi.org/10.1002/cssc.201402862>.
  - [45] Y. Liu, Y. Deng, Z. Sun, J. Wei, G. Zheng, A.M. Asiri, S.B. Khan, M.M. Rahman, D. Zhao, *Small* 9 (2013) 2702–2708, <https://doi.org/10.1002/sml.201300197>.
  - [46] I. Hwang, M. Baek, K. Yong, *ACS Appl. Mater. Interfaces* 7 (2015) 27863–27870, <https://doi.org/10.1021/acsami.5b09442>.
  - [47] J. Bharatvaj, V. Preethi, S. Kanmani, *Int. J. Hydrogen Energy* 43 (2018) 3935–3945, <https://doi.org/10.1016/J.IJHYDENE.2017.12.069>.
  - [48] C.-H. Lai, K.-W. Huang, J.-H. Cheng, C.-Y. Lee, B.-J. Hwang, L.-J. Chen, *J. Mater. Chem.* 20 (2010) 6638, <https://doi.org/10.1039/c0jm00434k>.
  - [49] S. Li, K. Yu, Y. Wang, Z. Zhang, C. Song, H. Yin, Q. Ren, Z. Zhu, *CrystEngComm* 15 (2013) 1753, <https://doi.org/10.1039/c2ce26692j>.
  - [50] H.G. Yang, C.H. Sun, S.Z. Qiao, J. Zou, G. Liu, S.C. Smith, H.M. Cheng, G.Q. Lu, *Nature* 453 (2008) 638–641, <https://doi.org/10.1038/nature06964>.
  - [51] M. El-Maazawi, A.N. Finken, A.B. Nair, V.H. Grassian, *J. Catal.* 191 (2000) 138–146, <https://doi.org/10.1006/jcat.1999.2794>.
  - [52] M. Salavati-Niasari, E. Esmaili, M. Sabet, *J. Clust. Sci.* 24 (2013) 799–809, <https://doi.org/10.1007/s10876-013-0575-2>.
  - [53] W. Du, L. Liao, L. Yang, A. Qin, A. Liang, *Sci. Rep.* 7 (2017) 1–12, <https://doi.org/10.1038/s41598-017-10904-y>.
  - [54] V. Augugliaro, S. Coluccia, V. Loddio, L. Marchese, G. Martra, L. Palmisano, M. Schiavello, *Appl. Catal. B* 20 (1999) 15–27, [https://doi.org/10.1016/S0926-3373\(98\)00088-5](https://doi.org/10.1016/S0926-3373(98)00088-5).
  - [55] M.C. Tsai, J.Y. Lee, P.C. Chen, Y.W. Chang, Y.C. Chang, M.H. Yang, H.T. Chiu, I.N. Lin, R.K. Lee, C.Y. Lee, *Appl. Catal. B* 147 (2014) 499–507, <https://doi.org/10.1016/j.apcatb.2013.09.033>.
  - [56] Q. Cao, R. Che, N. Chen, *Appl. Catal. B* 162 (2015) 187–195, <https://doi.org/10.1016/j.apcatb.2014.06.052>.
  - [57] Y. Liu, Y. Deng, Z. Sun, J. Wei, G. Zheng, A.M. Asiri, S.B. Khan, M.M. Rahman, D. Zhao, *Small* 9 (2013) 2702–2708, <https://doi.org/10.1002/sml.201300197>.
  - [58] Y. Lv, J. Chen, R.K. Zheng, J. Song, T. Zhang, X. Li, X. Shi, L. Chen, *Sci. Rep.* 5 (2015) 1–8, <https://doi.org/10.1038/srep16291>.
  - [59] Z. Khan, M. Khannam, N. Vinothkumar, M. De, M. Qureshi, *J. Mater. Chem.* 22 (2012) 12090, <https://doi.org/10.1039/c2jm31148h>.
  - [60] S.C. Riha, S. Jin, S.V. Baryshev, E. Thimsen, G.P. Wiederrecht, A.B.F. Martinson, *ACS Appl. Mater. Interfaces* 5 (2013) 10302–10309, <https://doi.org/10.1021/am403225e>.
  - [61] Z. Li, Z. Zhang, *Nano Res.* 11 (2018) 1530–1540, <https://doi.org/10.1007/s12274-017-1769-y>.
  - [62] M. Li, R. Zhao, Y. Su, Z. Yang, Y. Zhang, *Nanoscale* 8 (2016) 8559–8567, <https://doi.org/10.1039/c5nr06908d>.
  - [63] S. Liu, N. Zhang, Z.-R. Tang, Y.-J. Xu, *ACS Appl. Mater. Interfaces* 4 (2012) 6378–6385, <https://doi.org/10.1021/am302074p>.
  - [64] D. Praveen Kumar, N. Lakshmana Reddy, B. Srinivas, V. Durgakumari, V. Roddatis, O. Bondarchuk, M. Karthik, Y. Ikuma, M.V. Shankar, *Sol. Energy Mater. Sol. Cells* 146 (2016) 63–71, <https://doi.org/10.1016/J.SOLMAT.2015.11.030>.
  - [65] S. Wang, S. Yang, *Mater. Sci. Eng. C* 16 (2001) 37–40, [https://doi.org/10.1016/S0928-4931\(01\)00296-X](https://doi.org/10.1016/S0928-4931(01)00296-X).
  - [66] S. Wang, Q. Huang, X. Wen, X. Li, S. Yang, T.H. Kong, C.W. Bay, *Phys. Chem. Chem. Phys.* 4 (2002) 3425–3429, <https://doi.org/10.1039/b201561g>.
  - [67] N. Sakamoto, H. Ohtsuka, T. Ikeda, K. Maeda, D. Lu, M. Kanehara, K. Teramura, T. Teranishi, K. Domen, *Nanoscale* 1 (2009) 106–109, <https://doi.org/10.1039/b9nr00186g>.
  - [68] A. Pal, S. Srivastava, R. Gupta, S. Sapra, *Phys. Chem. Chem. Phys.* 15 (2013) 15888–15895, <https://doi.org/10.1039/c3cp51834e>.
  - [69] S. Rawalekar, S. Kaniyankandy, S. Verma, H.N. Ghosh, *J. Phys. Chem. C* 3 (2010) 1460–1466.
  - [70] X. Ma, K. Zhao, H. Tang, Y. Chen, C. Lu, W. Liu, Y. Gao, H. Zhao, Z. Tang, *Small* 10 (2014) 4664–4670, <https://doi.org/10.1002/sml.201401494>.
  - [71] J. Yu, L. Qi, M. Jaroniec, *J. Phys. Chem. C* 114 (2010) 13118–13125, <https://doi.org/10.1021/jp104488b>.
  - [72] H.J. Yun, H. Lee, N.D. Kim, D.M. Lee, S. Yu, J. Yi, *ACS Nano* 5 (2011) 4084–4090, <https://doi.org/10.1021/nn2006738>.
  - [73] N. Zhang, S. Liu, X. Fu, Y.-J. Xu, *J. Phys. Chem. C* 115 (2011) 9136–9145, <https://doi.org/10.1021/jp2009989>.
  - [74] D.P. Kumar, M.V. Shankar, M.M. Kumari, G. Sadanandam, B. Srinivas, V. Durgakumari, *Chem. Commun.* 49 (2013) 9443–9445, <https://doi.org/10.1039/c3cc44742a>.
  - [75] D.J. Martin, K. Qiu, S.A. Shevlin, A.D. Handoko, X. Chen, Z. Guo, J. Tang, *Angew. Chemie* 126 (2014) 9394–9399, <https://doi.org/10.1002/ange.201403375>.
  - [76] P. Ravi, V. Navakoteswara Rao, M. Sathish, *Int. J. Hydrogen Energy* 43 (2018) 3976–3987, <https://doi.org/10.1016/J.IJHYDENE.2017.08.213>.
  - [77] S. Guo, X. Li, J. Zhu, T. Tong, B. Wei, *Small* 12 (2016) 5692–5701, <https://doi.org/10.1002/sml.201602122>.
  - [78] Y. Zhang, Y. Tang, X. Liu, Z. Dong, H.H. Hng, Z. Chen, *Small* 7 (2013) 996–1002, <https://doi.org/10.1002/sml.201202156>.
  - [79] M. Xing, J. Zhang, B. Qiu, B. Tian, M. Anpo, M. Che, *Small* 11 (2015) 1920–1929, <https://doi.org/10.1002/sml.201403056>.
  - [80] X. Hao, Y. Wang, J. Zhou, Z. Cui, Y. Wang, Z. Zou, *Appl. Catal. B* 221 (2018) 302–311, <https://doi.org/10.1016/J.APCATB.2017.09.006>.
  - [81] V. Preethi, S. Kanmani, *Int. J. Hydrogen Energy* 43 (2018) 3920–3934, <https://doi.org/10.1016/j.ijhydene.2017.11.006>.
  - [82] P. Ruban, K. Sellappa, *Energy* 73 (2014) 926–932, <https://doi.org/10.1016/J.ENERGY.2014.06.107>.
  - [83] N. Buehler, K. Meier, J.F. Reber, *J. Phys. Chem.* 88 (1984) 3261–3268, <https://doi.org/10.1021/j150659a025>.